

Flow injection spectrophotometric determination of nitrate in electrolyte of lead–acid batteries

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Abstract

Electrolytes of lead–acid batteries can contain several impurities that reduce battery performance and lifetime. Nitrate ions are among these species because they can be reduced to ammonium in the lead electrode. In this work, an analytical method was developed to determine this anion in electrolytes of batteries used in telephone systems, in which nitrate concentration must be lower than 10 mg l^{-1} . The procedure consists in the reduction to nitrite in a copperized cadmium column followed by Griess's modified reaction. Due to the high sensitivity of this methodology, a large dispersion flow diagram (dispersion coefficient = 27.8) was projected. Thus, it was possible to eliminate the Schlieren effect and to obtain a $\text{NH}_3/\text{NH}_4^+$ buffer in the sample zone in a suitable pH for reduction reaction ($\text{pH} \cong 8$). Negative interference due to iron(III) was overcome by addition of excess iron (200 mg l^{-1}). A relocatable filter was used to remove iron(III) hydroxide precipitate. This avoided adsorption on the surface of the filings and increase of back pressure. The analytical frequency is 80 measurements/h and the detection limit was estimated as 0.3 mg l^{-1} in a 99.7% confidence level. A 2.2% relative standard deviation was obtained in a repeatability study ($n = 10$) by using a 25 mg l^{-1} nitrate solution in a 3.6 mol l^{-1} sulfuric acid medium. Recoveries from 95.5 to 104% were obtained by spiking 5.00 or 10.0 mg l^{-1} of nitrate in samples of battery electrolyte. © 1997 Elsevier Science B.V.

Keywords: Flow injection spectrophotometry; Lead–acid batteries; Nitrate; Refractive index; Schlieren effect

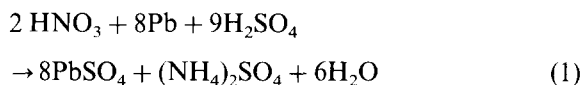
1. Introduction

Lead–acid batteries are useful devices to produce electrical energy from chemicals. This kind of battery is frequently employed in automobiles, electric vehicles, communication devices and to start engines. In the 1980s, lead–acid batteries represented approximately 60% of the sales of all batteries in the world [1]. The electrolyte in this

device is a sulfuric acid solution, with a concentration that depends on both charge state and application of the device. This solution can contain several impurities that affect performance and lifetime of the accumulator. In this sense, nitrate determination is important since this anion can be reduced to ammonium in the negative electrode (Eq. (1)). Thus, the active material of this electrode is consumed without supplying energy through the battery terminals. The formation of lead sulfate was measurable even in the pres-

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ence of low concentrations of nitrate [2], such as 10 mg l^{-1} . In addition, ammonium ions produced tend to accumulate during the aging of the battery and they can affect the performance of the device.



Most of the spectrophotometric methods for determining nitrate can be divided into three groups [3]: (1) nitration or oxidation of organic reagents, (2) measurements in the ultraviolet region, and (3) reduction to nitrite with subsequent determination of the reduced form by diazotization–coupling reactions. The first group involves methodologies that need high concentrations of sulfuric acid, and most of them are subject to interferences from nitrite, chloride and iron(III) ions [3]. The procedures based on measurements of nitrate in the ultraviolet region are very simple but the selectivity is poor. Several ions and organic substances that absorb radiation in the ultraviolet region are interferents [3]. Methods based on the reduction of nitrate are more reliable and selective than others. However, the reduction efficiency is pH dependent, and this must be considered to determine nitrate in the electrolyte of lead–acid batteries.

The procedure based on reduction of nitrate is more easily implemented by using flow injection analysis, since the reduction does not need to be quantitative. In addition, this useful technique for solution management can be explored to a pH adjustment from a previous reduction reaction. However, for relatively concentrated sulfuric acid solutions, the formation of intense refractive index gradients in the sample zone (Schlieren effect) can be troublesome. The usual way to overcome this perturbation is to employ a carrier with physical and chemical characteristics as similar as possible to the samples. However, in some situations this is not a practical alternative, such as the use of a relatively concentrated sulfuric acid solution as carrier for samples of electrolyte of lead–acid batteries.

Some experimental procedures can be used to avoid or to correct the Schlieren effect. An instrumental method based on measurements in two

wavelengths was proposed by Zagatto et al. [4]. These measurements must be equally affected by Schlieren effect in both wavelengths, and the molecular absorption process must only occur for one of them. Yamane and Saito [5] employed a flow diagram with injection of a large sample volume. Thus, the central part of the sample zone did not interact with the carrier, and measurements could be made in this region without perturbation. This is an ingenious way to overcome Schlieren effect when there is no limitation in available sample volume and the sampling frequency is not a critical aspect. The use of flow diagrams with large dispersion is the simplest alternative to avoid refractive index gradients, since in these systems the mixture between sample zone and carrier is improved [6]. Thus, a large dispersion flow diagram was investigated to determine nitrate in lead–acid batteries. In spite of the negative effect of dispersion on sensitivity, this procedure permits an adequate pH adjustment for reduction, and this improves the conversion rate of nitrate to nitrite.

2. Experimental

2.1. Apparatus

A peristaltic pump (Ismatec IPC-8) and Tygon tubes (Technicon) were used for fluid propulsion. Polyethylene tubing (0.8 mm i.d.) were used to set up the flow diagram. The absorbance was measured with a 432 Femto (São Paulo, Brazil) spectrophotometer equipped with a glass flow cell with a 0.86-cm optical path. A potentiometer recorder (Cole-Parmer) was used to register the transient signals. For injecting samples, a sliding bar commutator [7] was used. The filtration unit was a glass tube (1 cm; 3 mm i.d.) filled with glass wool.

2.2. Reagents and solutions

All solutions were prepared with analytical reagent grade distilled and deionized water. Sodium nitrate was dried at 110°C for 2 h and used for preparing nitrate stock solution, 1000 mg

l^{-1} . Work solutions were prepared by adequate dilution of this stock. Sulfuric acid additions were made from stock solutions containing 7.2 or 9.0 $mol\ l^{-1}$.

Chromogenic reagent (Griess's reagent) was prepared in the concentrations previously established for nitrate determination in natural waters [8], containing 2% (w/v) sulfanilamide and 0.1% (w/v) *N*-1-naphthylethylenediamine dihydrochloride in a 8.5% (v/v) phosphoric acid medium. Cadmium filings were copperized as formerly described [9] and packed into a glass tube (10 cm long; 3 mm i.d.) plugged with glass wool.

Buffer solutions were prepared containing 10, 20 or 25% (w/v) NH_4Cl and 0.5, 1.0, 2.0 or 4.0% (w/v) $Na_2B_4O_7 \cdot 10H_2O$. All solutions contained 0.1% (w/v) Na_2EDTA . Ammonium hydroxide solutions containing 3.0, 4.0, 5.0, 6.0 and 7.0 $mol\ l^{-1}$ were prepared from a stock solution (12.8 $mol\ l^{-1}$) standardized with a hydrochloric acid solution.

For investigating the effect of the iron(III) concentration on the analytical signal, nitrate solutions (10 $mg\ l^{-1}$) were prepared containing 2, 5, 10, 15, 20, 50, 100, 200 or 400 $mg\ l^{-1}$ iron(III) in a 3.6 $mol\ l^{-1}$ sulfuric acid medium.

Reference nitrate solutions (5.0, 10.0, 15.0, 20.0 and 25.0 $mg\ l^{-1}$) were prepared in a medium containing 3.6 $mol\ l^{-1}$ sulfuric acid and 200 $mg\ l^{-1}$ iron(III). Samples of electrolytes of lead–acid batteries were spiked with 5.00 or 10.0 $mg\ l^{-1}$ nitrate. A $2.5 \times 10^{-2}\ mol\ l^{-1}$ sulfuric acid solution was used to dissolve the iron(III) hydroxide precipitate in the system with the relocatable filter.

2.3. Flow diagrams and procedure

The flow diagram of the system with large sample dispersion is shown in Fig. 1. Some experiments were made without the filter (F) and employing only one section of the sliding bar commutator. Since mixing conditions are good, all measurements were made using water as carrier without refractive index perturbations. A 25- μl sample volume was inserted in the carrier by sliding the central part of the commutator. The sample was dispersed in the coil B_1 and confluent

streams of ammonium hydroxide and buffer solutions were introduced in the sample zone. The chromogenic reagent was introduced by confluence to the effluent of the cadmium copperized column. Absorbance measurements were made at 535 nm. The relocatable filter was used to remove the iron(III) hydroxide formed when solutions containing Fe^{3+} were processed. After the precipitate removal, the central part of the commutator is again slid and a sulfuric acid solution dissolves the solid in the filter.

3. Results and discussion

For determining nitrate in the electrolytes of lead–acid batteries by reduction to nitrite followed by diazotization–coupling reactions, the pH adjustment in the sample zone before reduction is essential. The merging zones approach was investigated with this purpose. Sample loops were filled with nitrate solutions prepared in 3.6 $mol\ l^{-1}$ sulfuric acid medium and with an alkaline solution (sodium or ammonium hydroxide). The best sensitivity was obtained with a 5 $mol\ l^{-1}$ ammonium hydroxide solution, because a buffer was formed in the sample zone with a suitable pH (ca. 8) to nitrite formation from nitrate by copperized cadmium. However, the repeatability was not good (R.S.D. = 13%; $n = 10$) due to the in-

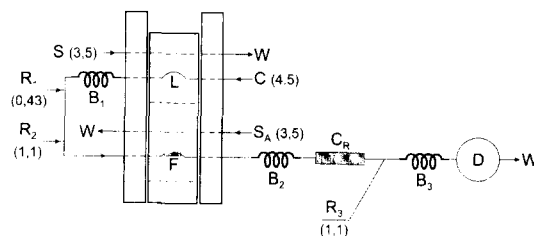


Fig. 1. Flow diagram of the system with large dispersion to nitrate determination. R_1 , R_2 and R_3 , indicate ammonium hydroxide, buffer and chromogenic reagent solutions, respectively. C, carrier (H_2O). B_1 is a dispersion coil. B_2 and B_3 are coiled reactors (50 and 200 cm, respectively). L, 5-cm sample loop (25 μl). C_R , copperized cadmium column (10 cm, 3 mm i.d.). D, spectrophotometric cell (535 nm). F, filter-glass tube (1 cm; 3 mm i.d.) filled with glass wool. S_A , 0.025 $mol\ l^{-1}$ sulfuric acid solution. W, waste. The numbers between brackets indicate flow rates in $ml\ min^{-1}$. For more details see text.

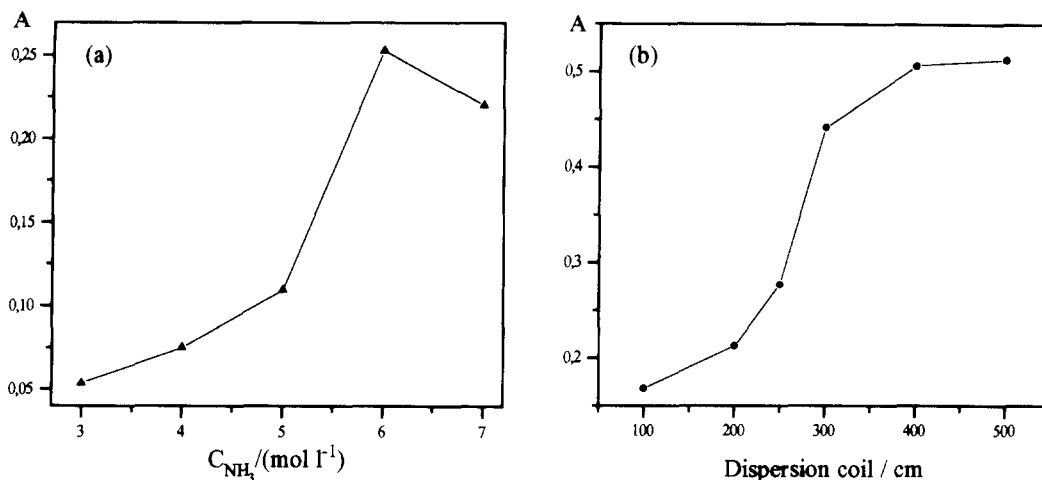


Fig. 2. Effect of (a) ammonium hydroxide concentration ($B_1 = 250$ cm) and (b) dispersion coil ($6 \text{ mol l}^{-1} \text{ NH}_3$) on the absorbance signals of nitrate in 3.6 mol l^{-1} sulfuric acid medium.

tense refractive index gradients in the sample zone and the high concentrations of salts formed by the acid–base reaction. Additionally, air bubbles were formed by the heating produced by the neutralization reaction.

To solve these problems, a large dispersion flow diagram was projected (Fig. 1, without filter F). This consisted in the reduction of the sample volume and employment of a large dispersion coil. Thus, sample zone dispersion was incremented before the confluent stream of ammonium hydroxide. The salt content in the sample zone and the heating produced by the neutralization reaction were decreased. Additionally, mixing conditions were improved and consequently the refractive index gradients were also decreased. With these modifications, a 0.9% relative standard deviation was obtained by using a 10 mg l^{-1} nitrate solution in a 3.6 mol l^{-1} sulfuric acid medium ($n = 10$). In spite of the large dispersion of the sample (dispersion coefficient = 27.8), the sensitivity losses were about 50%, because the reaction conditions (acidity and salt content) for nitrate reduction were improved.

The effects of the ammonium hydroxide concentration and of the length of the dispersion coil (B_1) were investigated, since they affect the acidity gradient in the sample zone and consequently the

conversion rate of nitrate to nitrite. The effects of these parameters are not independent and the best concentration of the alkaline solution depends on the length of the dispersion coil employed. Results obtained are shown in Fig. 2. The increase of the sensitivity is due to the pH adjustment for reduction of nitrate by the confluent addition of the alkaline solution (Fig. 2a) or the increase of sample dispersion (Fig. 2b). Relative to the effect of the ammonium hydroxide concentration, it was observed that the sensitivity was increased up to 6 mol l^{-1} solution (250-cm dispersion coil). When higher concentrations were employed with the same length of dispersion coil, the absorbance signal decreased. By maintaining this concentration, the length of the dispersion coil was changed and the best sensitivity was attained at $B_1 = 400$ cm. These parameters were employed in all subsequent studies.

With the formerly established conditions, the absorbance was very dependent on the acidity of the sample injected, and erroneous results were obtained when the sulfuric acid concentration in the samples was out of the $3.0\text{--}3.5 \text{ mol l}^{-1}$ range. To avoid this inconvenience, the effect of changing the composition of the buffer solution was evaluated. The effect of the ammonium chloride concentration was small for solutions varying

from 10 to 25% (w/v). For a 10% (w/v) NH_4Cl solution, the concentration of the $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ was changed from 0.5 to 4.0% (w/v). By using a 1.0% (w/v) tetraborate solution, samples with sulfuric acid concentration in the 3.0–4.5 mol l^{-1} range could be analyzed without errors caused by acid concentration effects. This concentration range is adequate for nitrate determination in samples of electrolyte of lead–acid batteries used in telephone systems.

For investigating the selectivity of the method, five samples were spiked with nitrate (from 2.00 to 8.00 mg l^{-1} , two additions in each one) and the concentrations were determined with the proposed system. For most samples, recoveries varied from 50 to 70%. For investigating the source of this negative error, concentrations of several species that can be found in sulfuric acid electrolytes (Al, Ca, Cd, Cr, Cu, Fe, Mg, Ni, Pb, Sb, Si, Sn and Zn) were estimated by ICP-AES. Most of these metals were not detected in any sample. However, some elements (Al, Ca, Fe and Zn) were present in many samples and the semi-quantitative results are shown in Table 1. Previous studies [9,10] indicated that zinc sulfate, aluminum sulfate, and calcium chloride (1% w/v) did not interfere in the nitrate determination when procedures similar to those proposed were employed. However, discrepant results were observed for iron. According to Henriksen and Selmer-Olsen [9], 1% (w/v) of ferrous sulfate or ferric chloride did not interfere in the nitrate determination. However, 0.5 $\text{mg Fe}^{3+} \text{ l}^{-1}$ caused serious interferences [11], and iron was cited as an

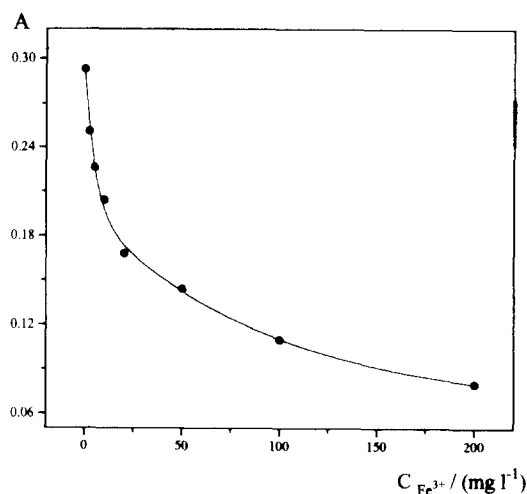


Fig. 3. Effect of iron(III) on the absorbance signals for nitrate (10 mg l^{-1}) in 3.6 mol l^{-1} sulfuric acid medium.

interferent in a standard method to determine nitrate in waters [12]. Thus, the effect of iron on the proposed method was investigated and the results obtained are shown in Fig. 3. It can be observed that the absorbance signal decreased exponentially with the iron concentration. For the concentrations determined in the samples investigated (Table 1), the analytical signal can decrease by up to 45%.

Davison and Woof [13] observed in a batch study employing an analogue procedure that several species caused interference in the determination of nitrate in fresh water. These drawbacks were ascribed to a kinetic effect on the nitrate reduction. In the presence of some concomitants, the reaction rate was reduced and the conversion rate become different to that observed for standard solutions. Probably, the perturbation due to iron(III) was caused by a similar effect. Since the residence time of the sample zone in the cadmium copperized column is very short (less than 8 s), iron(III) present in the samples could be reduced preferentially. Additionally, the nitrite produced could be oxidized by iron(III). Both effects could affect the global conversion rate of nitrate to nitrite.

Several procedures were investigated for eliminating the perturbation caused by iron(III), such

Table 1
Estimated concentrations of some metallic ions in electrolytes from batteries determined by ICP-AES

Sample	C (mg l^{-1})			
	Al	Ca	Fe	Zn
A	2.8	140	7.0	86
B	0.29	9.2	17	2.0
C	0.44	19	29	3.6
D	2.0	89	20	53
E	1.4	90	10	38
F	0.35	8.2	24	1.8

as employment of complexants (EDTA, fluoride, oxalate, phosphoric acid) or reductor agents (ascorbic acid, amalgamated zinc and stannous chloride) to iron(III). In spite of the interference decrement with some of these procedures, none was effective in eliminating it completely. The increase of the residence time in the column and the employment of a higher amount of reductor, as adopted in batch procedures to eliminate these perturbations [13], also produced unsatisfactory results. However, it can be seen in Fig. 3 that the rate of decrement of the analytical signal is less intense to higher concentrations of the ferric ion. This indicates that an addition of an excess of iron could be effective in leveling the perturbation. This was verified by additions of 200 or 400 mg l⁻¹ iron(III) in solutions containing 10 mg l⁻¹ nitrate in 3.6 mol l⁻¹ sulfuric acid and 0, 10, 20 or 50 mg l⁻¹ iron(III). Results obtained are shown in Table 2. It can be verified that 200 mg l⁻¹ was effective in leveling the perturbation. In spite of the decrease of the absorbance signal, the sensitivity is enough to determine nitrate in electrolytes of lead–acid batteries.

By addition of an excess of the interfering ion, the precipitation of iron(III) hydroxide in the sample zone after the pH adjustment was observed. The adsorption of the precipitate on the surface of the filings affected the reduction efficiency and caused an increase of the back pressure. To avoid this drawback, a filter was inserted in the system (see Fig. 1). The relocation of this component such as formerly employed [14] was adequate to remove and dissolve the precipi-

Table 2

Effect of iron(III) addition on the interference caused by iron in the absorbance of 10 mg l⁻¹ nitrate in 3.6 mol l⁻¹ sulfuric acid medium

Iron (sample) (mg l ⁻¹)	Iron (added) (mg l ⁻¹)		
	0	200	400
0	0.475 ± 0.004	0.048 ± 0.002	0.006 ± 0.001
10	0.373 ± 0.003	0.049 ± 0.001	0.006 ± 0.001
20	0.321 ± 0.004	0.049 ± 0.001	0.006 ± 0.001
50	0.263 ± 0.001	0.045 ± 0.002	0.006 ± 0.001

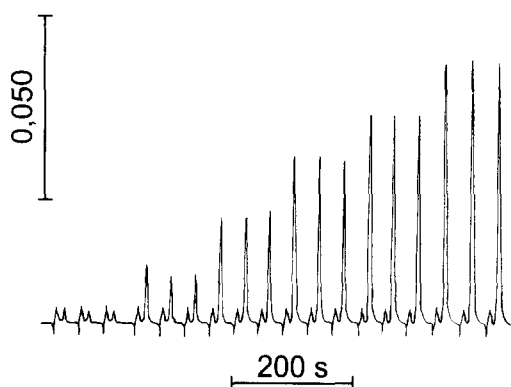


Fig. 4. Absorbance signals obtained for reference nitrate solutions (0, 5.00, 10.0, 15.0, 20.0 and 25.0 mg l⁻¹) in a 3.6 mol l⁻¹ sulfuric acid medium. Flow diagram as in Fig. 1.

tate. Despite the precipitation of iron(III) hydroxide, the remaining iron concentration in the sample zone was enough to level off the perturbation.

Nitrate can be properly determined in electrolyte samples containing from 3.0 to 4.5 mol l⁻¹ H₂SO₄ without perturbation due to the Schlieren effect by using the system shown in Fig. 1, with a 400-cm dispersion coil (B₁), 6 mol l⁻¹ ammonium hydroxide (R₁), and a buffer (10% (w/v) NH₄Cl, 1.0% (w/v) Na₂B₄O₇ · 10H₂O) containing 0.1% (w/v) Na₂EDTA. The addition of 200 mg l⁻¹ of iron(III) is necessary to level off the perturbation and a relocatable filter is employed to remove the hydroxide precipitate.

Using this system, a repeatability study was performed and a 2.0% relative standard deviation was obtained (*n* = 10) with a solution containing 25 mg l⁻¹ nitrate in 3.6 mol l⁻¹ sulfuric acid medium. According to the diagram in Fig. 4, the absorbance signal (*A*) can be related with the concentration (*C*, mg l⁻¹) by the equation: $A = 0.00286 + 0.00675C$ (*r* = 0.999). The signal distortion observed before the analytical transient signal for nitrate is due to the refractive index gradient caused by the introduction of the sulfuric acid solution remaining in the filter after removal of the precipitate. However, this does not affect the measurements.

The detection limit was estimated in 0.3 mg l⁻¹ (99.7% confidence level) and the sampling rate

Table 3

Addition–recovery of nitrate in electrolytes from lead–acid batteries

Sample	Nitrate (mg l ⁻¹)		Recovery (%)
	Added	Found	
1	5.00	5.00	100
	10.0	9.55	95.5
2	5.00	5.15	103
	10.0	9.91	99.1
3	10.0	10.4	104
4	10.0	9.61	96.1
5	10.0	9.70	97.0

was 80 h⁻¹. An addition–recovery test was performed by spiking samples of electrolyte of lead–acid batteries with 5.00 or 10.0 mg l⁻¹ nitrate. The results obtained are shown in Table 3. Recoveries between 95.5 and 104% are adequate to determine nitrate in the samples. Additional studies of accuracy were not possible because standard reference materials or standard reference methods are not available. The comparison with other procedures for nitrate determination was not made, since these could not be directly applied to the electrolyte of batteries or they suffered from lack of selectivity.

4. Conclusions

The proposed method is adequate for rapid determination of nitrate in electrolytes of lead–acid batteries. Interference due to iron(III) was leveled off by addition of excess of the interfering ion, and the iron(III) hydroxide was properly removed and dissolved by using a relocatable filter. A large dispersion flow diagram was effective to eliminate the Schlieren effect, and similar approaches could be used to determine other spe-

cies in matrices characterized by the presence of high concentrations of concomitants.

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